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Vacancy-mediated hydrogen desorption in NaAlH₄

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First-principles calculations based on density functional theory are carried out to understand the mechanisms responsible for hydrogen desorption from Ti-doped sodium-alanate (NaAlH₄). While the energy needed to remove a hydrogen atom from NaAlH₄ with Ti substituted either at the Na site or at Al site is found to be significantly lower than that from the pristine NaAlH₄, the presence of Na vacancies is shown to play an even larger role: It is not only an order of magnitude smaller than that from Ti-doped sodium-alanate, but the removal of hydrogen associated with a Na vacancy is exothermic with respect to formation of H₂ molecule. Furthermore, we show that the unusual stabilization of the magic AlH₃ cluster in the vacancy containing sodium-alanate is responsible for this diminished value of the hydrogen-removal energy. It is suggested that this role of vacancies can be exploited in the design and synthesis of complex light-metal hydrides suitable for hydrogen storage.

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I. INTRODUCTION

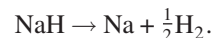
The growing worldwide demand for energy, the limited supply of fossil fuels, and their adverse effect on the environment have made it necessary to search for alternative energy sources that are renewable, abundant, secure, environmentally friendly, and cost effective.¹ One of the alternate energy resources that are currently being pursued involves hydrogen.²⁻⁷ Although hydrogen is among the most abundant elements on earth, exhibits the highest heating value per mass of chemical fuels, and is pollution free as water is the only by-product during combustion, there are numerous hurdles to overcome in its production, distribution, storage, and use in fuel cells. Among these, hydrogen storage is considered to be the biggest challenge in a new hydrogen economy⁸ since the storage medium must meet the requirements of high gravimetric (~10 wt %) and volumetric density, fast kinetics, and favorable thermodynamics. Currently there are no storage media that meet simultaneously all of the above requirements.

The current methods for storing hydrogen in gaseous form under high pressure or in liquid form in cryogenic tanks are problematic. First, there are concerns with safety and cost in compressing and liquefying the hydrogen gas. Second, the energy densities of hydrogen under 10 000 psi (4.4 MJ/L) and liquid hydrogen at 20 K (8.4 MJ/L) are significantly smaller than that in gasoline (31.6 MJ/L). The solid-state storage of hydrogen offers an alternate choice⁹ since in certain intermetallics the density of hydrogen can exceed that of its liquid state. More importantly, hydrogen absorption and desorption in these materials can take place under ambient conditions. Unfortunately, the gravimetric densities of hydrogen in these intermetallics seldom exceed 3 wt % (Ref. 9) and the materials are not suitable for practical applications.

It is easy to see that for a material to store hydrogen at around 10 wt %, it has to consist of light elements such as Li, B, N, C, Na, Mg, and Al. However, hydrogen in these materials is held by strong covalent or ionic bonds. Consequently, the hydrogen desorption temperatures are high and

the kinetics is slow. Ideally hydrogen should be stored in such a way that it is neither easy (as would be the case if they are molecularly physisorbed) nor difficult for it to desorb (as would be the case if hydrogen is held in strong covalent or ionic bonds) at moderate temperatures. The central challenge then is to find materials that can store hydrogen like methane but whose kinetics and thermodynamics mimic that of intermetallics.

Recently a great deal of attention has been focused on complex light-metal hydrides and in particular on sodium-alanate (NaAlH₄), due to their high hydrogen content.¹⁰⁻²⁵ Here the four hydrogen atoms form a tetrahedron that encapsulates an Al atom (much as in methane) and the AlH₄ unit is stabilized by the transfer of one electron from the Na atom. The four hydrogen atoms are covalently bonded to Al while the (AlH₄)⁻ unit is bonded to Na⁺ by an ionic bond. Desorption of hydrogen takes place in the following three steps:



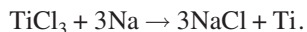
The first reaction releases 3.7 wt % of hydrogen, while the second one releases 1.9 wt % relative to the starting material NaAlH₄. The third step requires very high temperature and thus the hydrogen-storage capacity of sodium alanate is considered to be 5.6 wt %. The addition of small amount of TiCl₃ to sodium-alanate was found not only to make the above process reversible, but also to markedly lower the hydrogen desorption temperature.¹⁰ This discovery has revitalized the research into complex light-metal hydrides as potential hydrogen-storage materials. Moreover, the role of catalysts has been highlighted.¹¹ In spite of this interest, a full understanding of where Ti resides and how it helps to lower the hydrogen-desorption temperature is lacking.

Several experiments¹²⁻¹⁸ have been carried out to study the location of Ti in sodium-alanate, but they have yielded conflicting results. While in some experiments Ti has been

found to remain on the surface,^{10,17} in others Ti is found to occupy the bulk Na site.^{14,20} Experimental evidence also exists where Ti combines with Al to form TiAl_3 and segregates to the zone boundary.¹⁶ The energetics of these different scenarios have not been studied yet.

Theoretical studies of NaAlH_4 and Ti-doped NaAlH_4 clusters and crystals have been recently carried out using density functional theory.^{20,24,25} All calculations show that NaAlH_4 is an insulator, the bonding between Al and H atoms is covalent, and due to charge transfer from Na to AlH_4 , Na^+ and $(\text{AlH}_4)^-$ bind ionically. However, the site preferred by Ti has been controversial. Iniguez *et al.*²⁰ showed that Ti prefers to occupy the Na site while Lovvik and Opalka²⁰ argue that the least unfavorable site for Ti is that of Al. This difference arises due to the reference energies one uses. Iniguez *et al.* have chosen this reference to be isolated atoms while Lovvik and Opalka have used bulk cohesive energies of Ti, Al, and Na as reference. We have shown that in both cases the bonding of hydrogen to metal atoms is weakened and the energy necessary to remove a hydrogen atom is consistently lower than that from pristine sodium alanate irrespective of whether Ti occupies the Na or the Al site.²⁵ For example, the energy necessary to remove a hydrogen atom from pure NaAlH_4 is 4.0 eV, while it is only 1.9 eV when Ti occupies a Na site and 2.5 eV when Ti occupies the Al site. The lowering of the hydrogen desorption temperature is attributed to this reduction in the hydrogen-removal energy.

It should be noted that formation of NaCl has also been observed during ball milling of NaAlH_4 with TiCl_3 .¹⁶ This could happen through the following reaction:



Thus, for every TiCl_3 that combines with Na to form NaCl , three Na vacancies can be created. Even if the Ti atom is an occupier of one of these Na-vacant sites, two Na vacancies will still remain in the sample. The effect of these vacancies on the hydrogen desorption has not been considered yet.

In this paper we have addressed this issue. We show that these vacancies can play a dominant role in the hydrogen-desorption process. In particular, we show that the energy needed to remove an H atom from sodium-alanate containing a Na vacancy is only 0.2 eV—a factor of more than 5 smaller than that associated with a Ti substitution. This result is consistent with recent experiments²⁶ where hydrogen desorption was observed to occur at lower temperatures in ball-milled samples of sodium-alanate without the presence of catalysts. Note that during ball milling, point defects such as vacancies can be introduced. Furthermore, we show that the unusual stabilization of the magic AlH_3 cluster is responsible for such a small value of the hydrogen-removal energy. In Sec. II we outline our computational procedure. The results are discussed in Sec. III and summarized in Sec. IV.

II. COMPUTATIONAL PROCEDURE

Our calculations are carried out within the framework of density functional theory²⁷ using the PAW method,²⁸ as implemented in the VASP code.²⁹ PAW potentials with valence states $2p$ and $3s$ for Na, $3s$ and $3p$ for Al, and $1s$ for H

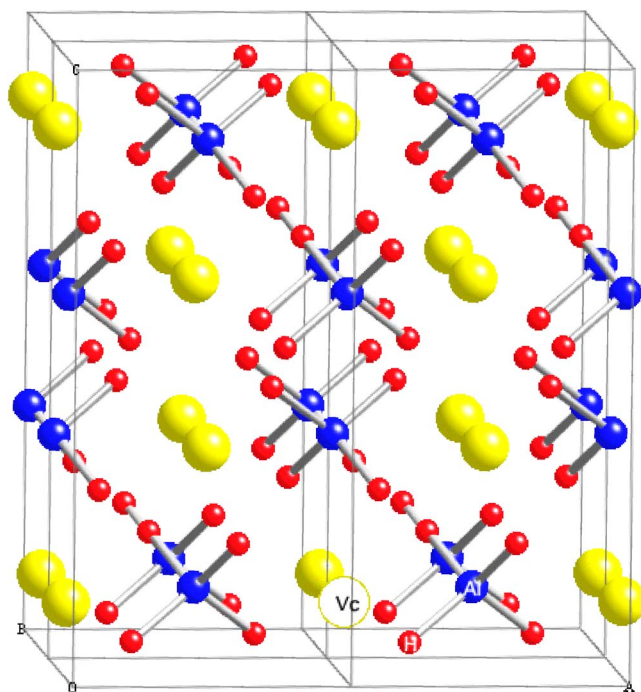


FIG. 1. (Color online) The 96-atom supercell geometry of $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$. The yellow, blue, and red color atoms correspond to Na, Al, and H, respectively. The Na vacancy is marked by Vc, and the hydrogen removed in the calculation is marked by H.

were used. We have chosen an energy cutoff of 500 eV. In order to calculate the cohesive energy of the H_2 molecule, we have used a cubic supercell with large lattice parameter (chosen to be 21 Å), which guarantees a small intermolecular interaction. In this calculation we have used both the local-density approximation (LDA) and the generalized gradient approximation (GGA).³⁰ The latter yields a cohesive energy of -4.57 eV, which agrees better with the experimental value of -4.75 eV (Ref. 31) than that obtained using the LDA—namely, -5.07 eV. This result is consistent with some previous theoretical investigations where the LDA has overestimated the cohesive energy of molecules and solids.^{32,33} Based on this finding, we have chosen the GGA functional for all other calculations. We should emphasize that it is important to use the spin polarization formalism in the calculation of the energy of the H atom without which the cohesive energy of the H_2 molecule is found to be -6.787 eV. This is in agreement with the value of -6.781 eV, which has been calculated recently by Ke and Tanaka.³⁴ The electronic densities of states (DOS) were calculated by means of the modified tetrahedral method of Blöchl *et al.*³⁵ and the electron localization functions (ELF) were calculated according to Ref. 36.

In order to study the effect of a Na-vacancy formation on hydrogen desorption, we have first constructed a $(2 \times 2 \times 1)$ supercell consisting of 96 atoms ($\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$). This is shown in Fig. 1. The optimization of the supercell has been done (ionic coordinates and c/a ratio) without any symmetry constraint using the Hellmann-Feynman forces on the atoms and stresses on the supercell. For sampling the irreducible wedge of the Brillouin zone we have used the \mathbf{k} -point grids of $3 \times 3 \times 3$ for the geometry optimization and $5 \times 5 \times 5$ for

the final calculation at the equilibrium volume. In all calculations, self-consistency was achieved with a tolerance in the total energy of at least 0.1 meV. The calculated lattice constants $a=4.95$ Å and $c=10.89$ Å as well as the Na-Al and Al-H distances of 3.50 Å and 1.64 Å compare very well with the corresponding experimental values of 4.98 Å, 11.15 Å, 3.52 Å, and 1.63 Å.³⁷ The Na vacancy is simulated by using the Na₁₅Al₁₆H₆₄ supercell. In Fig. 1 the Na-vacant site is denoted as “Vc”. The optimization of all the atomic coordinates in the Na₁₅Al₁₆H₆₄ supercell was carried out using the same procedure as discussed above. It should be pointed out that we are considering here the simple case of a neutral vacancy, which does not require any charge background. The energies needed to remove a hydrogen atom from these supercells were calculated by reoptimizing the atomic coordinates in the Na₁₆Al₁₆H₆₃ and Na₁₅Al₁₆H₆₃ supercells and calculating the respective cohesive energies. The hydrogen atom removed to form these supercells is identified as “H” in Fig. 1.

III. RESULTS AND DISCUSSIONS

We first discuss the relaxation of the atomic positions following the removal of a Na atom. In the perfect sodium alanate crystal the distance between nearest Na and Al is 3.50 Å while that between Al and nearest four hydrogen atoms is 1.64 Å. As a Na atom is removed, one would expect the nearest Al atom to move toward the vacant site and the Al-H distances to change. This is because the creation of a Na vacancy will deprive the nearest (AlH₄)⁻ unit from the extra electron that it needs for being stabilized in the tetrahedral form. It is known from cluster calculations that the neutral AlH₄ cluster is unstable against dissociation into AlH₂ and H₂ molecule.²⁴ To our surprise, we find very little structural change after relaxation. The distance between the Na-vacant site and its nearest Al neighbor reduces to 3.47 Å, and the four hydrogen atoms bound to the Al atom remain at distances of 1.62 Å, 1.64 Å, 1.64 Å, and 1.65 Å. Thus there is very little structural relaxation associated with the creation of a Na vacancy. This could be due to the fact that the atoms nearest to the Na vacancy in the sodium-alanate crystal are bounded by other units that are held with strong covalent or ionic bonds while in a free AlH₄ cluster such an environment does not exist. We will show in the following that the hydrogen-removal energy is significantly altered as a result of the Na vacancy even though the lattice does not distort.

We now compare the energy needed to remove a hydrogen atom from both the intrinsic crystal and the one containing a Na vacancy. In order to do that, we first calculate the cohesive energy of the Na₁₆Al₁₆H₆₄, Na₁₅Al₁₆H₆₄, Na₁₆Al₁₆H₆₃, and Na₁₅Al₁₆H₆₃ supercells. This energy is defined as the total energy of the system minus the sum of individual atomic energies. The hydrogen-removal energies are thus defined as

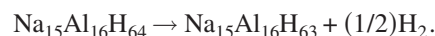
$$\Delta E_0 = E_{\text{coh}}[\text{Na}_{16}\text{Al}_{16}\text{H}_{63}] - E_{\text{coh}}[\text{Na}_{16}\text{Al}_{16}\text{H}_{64}],$$

$$\Delta E_V = E_{\text{coh}}[\text{Na}_{15}\text{Al}_{16}\text{H}_{63}] - E_{\text{coh}}[\text{Na}_{15}\text{Al}_{16}\text{H}_{64}].$$

The energy needed to remove a hydrogen atom from pristine NaAlH₄ (ΔE_0) is 4.0 eV. This large value is a consequence

of the strong covalent bonds that are holding the H atoms. The energy needed to remove a hydrogen atom from the vicinity of a Ti atom substituted at a Na site was found to be 1.9 eV.²⁵ This is due to the change in the electronic structure caused by Ti substitution as can be seen from both the ELF and the electronic DOS. It was shown that Ti weakens the strength of the covalent bond between Al and H, thus reducing the energy necessary to remove a hydrogen atom. This is also consistent with the structural changes where the Al-H bond length in the TiNa₁₅Al₁₆H₆₄ supercell increased from 1.64 Å to 1.70 Å. Furthermore, the energy needed to remove a hydrogen atom in the vicinity of Ti substituted at Al site is also smaller than that in the perfect crystal; it was found to be 2.5 eV. This is due to the metallic bonding between Ti and H.

The creation of a Na vacancy plays a dramatic role on the hydrogen-removal energy: It costs only 0.2 eV (ΔE_V) to take away the hydrogen atom nearest to the Na-vacant site in the Na₁₅Al₁₆H₆₄ supercell. This is more than a factor of 5 smaller than that when Ti is substituted at the Na site in sodium-alanate and one order of magnitude smaller than that in the intrinsic sodium-alanate. Furthermore, dictated by the fact that hydrogen atoms are desorbed associatively forming a hydrogen molecule, we have also calculated the energy difference in the following reaction;



It is achieved by adding half of the H₂ cohesive energy [$E_{\text{coh}}(\text{H}_2)$] to ΔE_V . $E_{\text{coh}}(\text{H}_2)$ was calculated as described in Sec. II. The energy difference in the above reaction is thus found to be -2.1 eV. The negative sign means that the removal of a hydrogen atom from the vicinity of a Na-vacant site is exothermic with respect to formation of H₂ molecule. However, for this process to occur, one must invest 0.2 eV for the removal of each hydrogen atom. Thus the process can only occur at elevated temperatures. This is in agreement with recent experiments.²⁶

Our task is now to understand the origin of this substantial reduction in the hydrogen-removal energy following the creation of a Na vacancy. The initial thinking was that the presence of a Na vacancy deprives the adjacent AlH₄ unit from the extra electron that it needs for stabilization. However, as discussed previously, the structure of AlH₄ unit adjacent to the Na vacancy [see Fig. 2(b)] is nearly the same as that in NaAlH₄ [see Fig. 2(a)].

To understand this paradox, we show in Figs. 2(c) and 2(d) the geometries of the AlH₃ units following the removal of a H atom from the Na₁₆Al₁₆H₆₄ and Na₁₅Al₁₆H₆₄ supercells, respectively. Note that while the bonding between Al and H in the AlH₃ unit in the Na₁₆Al₁₆H₆₃ supercells remains nearly tetrahedral, that in the Na₁₅Al₁₆H₆₃ supercell is very different—namely, it is nearly planar with an Al-H bond length of 1.61–1.62 Å. We have seen from earlier calculations on AlH_n clusters²⁴ that the geometry of the AlH₃ cluster is planar and that the Al-H bond lengths are 1.60 Å. In addition, AlH₃ is a magic cluster (i.e., the most stable among the AlH_n series) since the energy gained in forming AlH₃ from AlH₂ is 3.56 eV, while that in forming AlH₄ from AlH₃ is only 1.13 eV.²⁴ It is this unusual stability of the planar

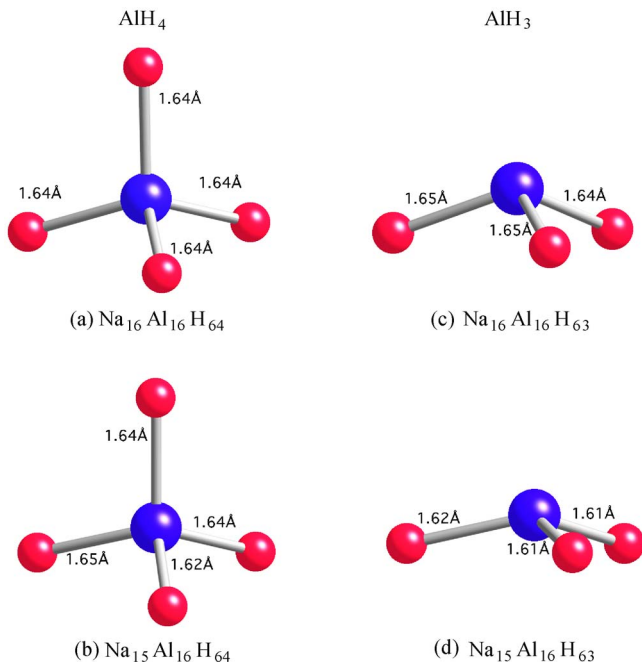


FIG. 2. (Color online) The geometries of the AlH_4 complexes in (a) $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$ and (b) $\text{Na}_{15}\text{Al}_{16}\text{H}_{64}$ supercells and those of AlH_3 complexes in (c) $\text{Na}_{16}\text{Al}_{16}\text{H}_{63}$ and (d) $\text{Na}_{15}\text{Al}_{16}\text{H}_{63}$ supercells.

AlH_3 cluster that is primarily responsible for the reduced hydrogen removal energy from the $\text{Na}_{15}\text{Al}_{16}\text{H}_{64}$ supercell. Thus, the role of vacancy manifests in the formation of a stable AlH_3 unit following the H desorption.

This picture can be further established by investigating the effect of the Na vacancy on the electronic structure of sodium alanate. It is done through the analysis of the ELF as well as the DOS. The former has been recognized as a powerful tool to visualize different types of bonding in solids and molecules.^{36,38,39} According to its definition, the ELF can assume values in the range 0–1, where 1 corresponds to perfect localization and 0.5 to the case of uniform gas. In Fig. 3(a) we display the two-dimensional distribution of ELF on the (001) plane for the intrinsic crystal. One can observe the high ELF within the AlH_4^- unit, which confirms the expected covalent bonding between H and Al atoms. The very low value of the ELF between AlH_4^- and Na^+ reflect its ionic bonding. The ELF profile changes very little when a Na vacancy is created [see Fig. 3(b)]. For example, the nature of bonds between Na, Al, and H remains nearly the same as in the perfect crystal. Such a result can also be confirmed from the DOS picture. In Fig. 4, we show the calculated *s* and *p* partial DOS for Na, Al, and H atoms in the $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$ supercell. The valence band is split into two regions. The low-energy region is composed of Al 2*s* and H 1*s* states, whereas the high-energy region is composed mainly by hybridization between Al 2*p* and H 1*s* states. This result is consistent with the directional covalent bond between the aluminum and hydrogen atoms discussed earlier. The bottom of the conduction band just above the Fermi energy is primarily composed of the Na *p* and *s* antibonding states. This is consistent with the ionic bonding between Na^+ and $(\text{AlH}_4)^-$ units. The calculated *s* and *p* partial DOS for Al and H atoms belonging to the AlH_4 unit nearest to the Na-vacant

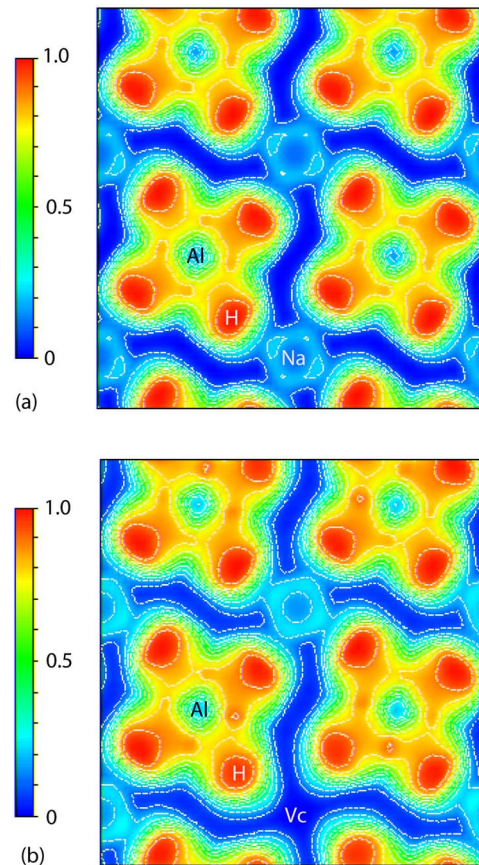


FIG. 3. (Color online) The two-dimensional distribution of electron localization function (ELF) on (001) plane for both (a) $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$ and (b) $\text{Na}_{15}\text{Al}_{16}\text{H}_{64}$ supercells.

site in the $\text{Na}_{15}\text{Al}_{16}\text{H}_{64}$ supercell are shown in Fig. 5. They are basically the same as that in the $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$ supercell described above. The valence band is dominated by Al- and H-hybridized states. This is consistent with the small relaxation of the AlH_4 cluster adjacent to the Na-vacancy site

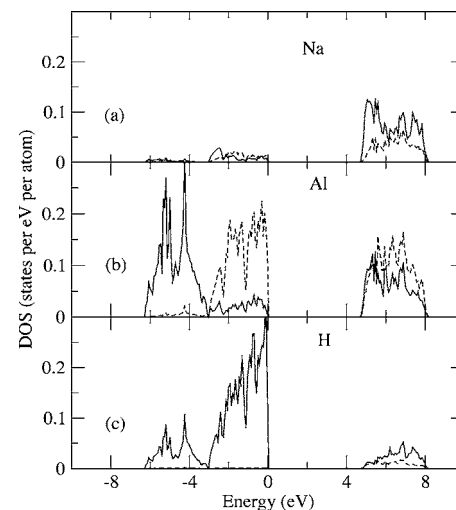


FIG. 4. Partial density of states of (a) Na, (b) Al, and (c) H atom in the $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$ supercell. The solid and dashed lines denote *s* and *p* states, respectively.

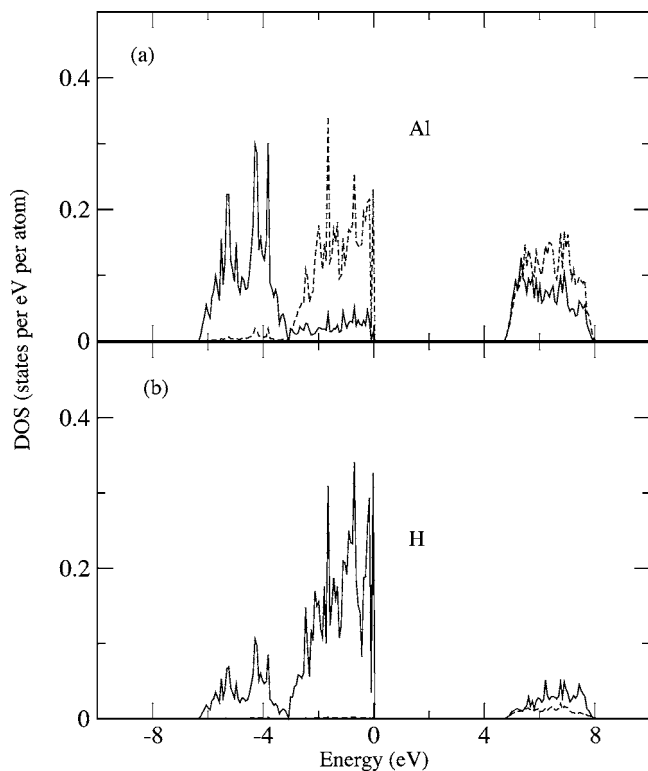


FIG. 5. Partial density of states of (a) Al and (b) H atom adjacent to the Na-vacancy site in the Na₁₅Al₁₆H₆₄ supercell. The solid and dashed lines denote *s* and *p* states, respectively.

discussed earlier. So far, electronic structure analyses have shown that the role of Na vacancies in lowering the hydrogen-removal energy is not associated with the weakening of the strength of covalent bonding between Al and H, as it is for Ti atoms.^{20,25}

It is interesting to compare now the partial DOS of Al and H atoms in the AlH₃ cluster in the Na₁₅Al₁₆H₆₃ supercell (see Fig. 6) with the correspondent ones presented in Fig. 5—i.e., in the Na₁₅Al₁₆H₆₄ supercell. One can observe the formation of some new states in the low-energy region around -6 eV, making the valence band broader than that composed by Al and H states in the AlH₄ unit. It means that energy is gained in the formation of AlH₃ clusters in the vicinity of a Na-vacant site in the Na₁₅Al₁₆H₆₄ supercell. This is consistent with the calculations of AlH_{*n*} (*n*=1–4) clusters,²⁴ which show that AlH₃ is the most stable cluster in this series. Such a result supports our conclusion that the unusual stabilization of the magic AlH₃ cluster plays an important role in lowering the hydrogen-removal energy in sodium-alanate containing Na vacancies.

IV. CONCLUSIONS

In summary, we have used the density functional theory and supercell approach to study the electronic structure and hydrogen-removal energies associated with a Na vacancy in

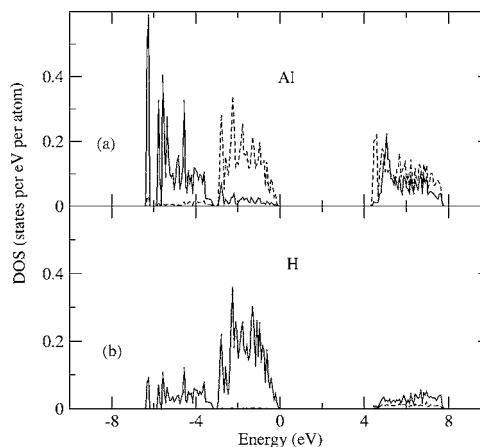


FIG. 6. Partial density of states of (a) Al and (b) H atom adjacent to the Na-vacancy site in the Na₁₅Al₁₆H₆₃ supercell. The solid and dashed lines denote *s* and *p* states, respectively.

NaAlH₄. The results are compared with those when a Ti atom occupies either a Na or an Al site. The energy needed to remove a hydrogen atom from the TiNa₁₅Al₁₆H₆₄ (Na₁₆TiAl₁₅H₆₄) supercell is 1.9 eV (2.5 eV),²⁵ while that from the Na₁₆Al₁₆H₆₄ supercell is 4.0 eV. We have found that the presence of a Na vacancy plays an even larger role in the hydrogen desorption. The hydrogen-removal energy in this system (Na₁₅Al₁₆H₆₄) is 0.2 eV, which is an order of magnitude smaller than that in the perfect crystal. More importantly, this process can be exothermic since the two desorbed hydrogen atoms can combine to form a H₂ molecule and contribute nearly 2.3 eV/H atom of energy into the system. We have neglected the effect of temperature and, in particular, the vibration and configuration entropy in our calculations. Recently, Watari *et al.*⁴⁰ have calculated the configuration entropy in Pd-hydrogen clusters and found it to be 0.05 eV. This small contribution will not affect our results. We conclude that the dominant role of Ti in reducing the hydrogen-desorption temperature may be an indirect one—it leads to vacancy formation which then reduces the hydrogen-desorption energy. More importantly, it is shown that the unusual stabilization of the magic AlH₃ cluster, allowed by the presence of a Na vacancy, is responsible for the lowering of the hydrogen-removal energy. This work suggests that a catalyst suitable to reduce the hydrogen-desorption temperature may be the one that can easily create vacancies in the alanates. We hope that this new mechanism will stimulate further experimental work.

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